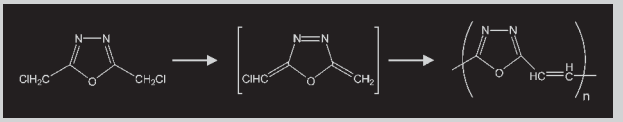
Communication: 2,5-Bis(chloromethyl)-1,3,4-oxadiazole was synthesized and dehydrohalogenation of this model compound was investigated under various base conditions. The formation of an intermediate with quinodimethane-type structure is suggested for reaction in EtONa/EtOH. Polymerization of this intermediate proceeds via an anionic mechanism to form poly(1,3,4-oxadiazole-2,5-diyl-1,2-vinylene). Polymerization at a toluene/water interface results in shorter polymerization times, milder conditions, higher molecular weights, higher yields and fewer defects in the polymer as compared to the corresponding polycondensation route.



Preparation of Poly(1,3,4-oxadiazole-2,5-diyl-1,2-vinylene) via Anionic Mechanism

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Introduction

The polymerization of bis(halomethyl)benzenes in the presence of a large excess of potassium *tert*-butoxide to poly(*p*-phenylene vinylene)s (PPV) is referred to as the Gilch route.[1] Recently, the Gilch route has been widely used for the preparation of soluble PPV derivatives[2–7] as well as poly(*p*-xylylene).[8,9] It has been generally accepted that the Gilch route involves the polymerization of an active intermediate, 1,4-quinodimethane, which is generated by base-induced dehydrohalogenation of bis(halomethyl)benzenes or 4-halomethyltoluenes. It is still under discussion, whether polymerization proceeds via an anionic mechanism or with a biradical species as an intermediate.[10]

Formally, the active intermediate can be regarded as an aromatic moiety, inserted into a double bond (see Scheme 1). In order to re-establish an aromatic system from the conjugated α,ω-elimination product (dehydrohalogenation), the intermediate will exhibit high reactivity to polymerize either via anionic or free-radical mechanism.

In known reaction systems that are related to the Gilch route, only electron-rich aromatic moieties such as benzene and alkoxybenzenes have been used. It might also be possible, to ''insert'' an electron-poor unit, i.e. 1,3,4-oxadiazole, into the double bond of vinyl chloride. Such an intermediate should be similar to quinodimethane, and would result in the formation of poly(1,3,4-oxadiazole-2,5-diyl-1,2-vinylene) as an electron-poor PPV analog. The different aromatic unit should have a significant impact onto the polymerization mechanism. An alternative synthetic route toward this polymer might be helpful because to date, poly(1,3,4-oxadiazole-2,5-diyl-1,2-vinylene) can only be prepared by polycondensation of fumaramide with hydrazine sulfate in polyphosphoric acid,[11] resulting in rather low-molecular-weight polymers featuring the inevitable problems of structural defects. As a first step, a new model compound, 2,5-bis(chloromethyl)-1,3,4-oxadiazole, was synthesized and the dehydrohalogenation was studied under various base conditions.

Experimental Part

Materials

Chloroacetyl chloride, hydrazine hydrate, sodium carbonate, perchloric acid (70%), sodium ethoxide, tetrabutylphosphonium bromide, potassium hydroxide and absolute ethanol were used as received (Aldrich). All solvents were used as received.

Measurements

^{1}H NMR spectra were recorded on a Bruker ARX 300 spectrometer. Infrared spectra were recorded on a Bruker IFS 55s FT-IR spectrometer using KBr pellets for solid samples and NaCl single crystal plates for liquid samples.

1,2-Dichloroacetylhydrazine

A 500 ml flask equipped with condenser was charged with 20.1 g (0.4 mol) hydrazine hydrate and 50 ml diethyl ether. To

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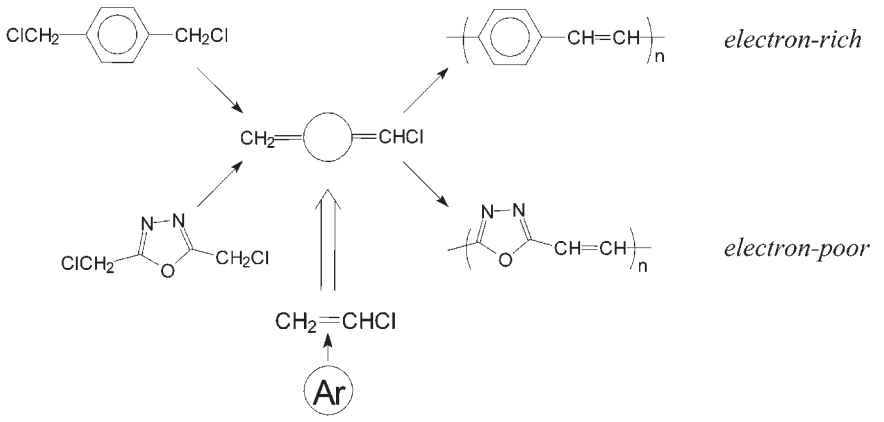


Scheme 1.

this mixture, a solution of chloroacetyl chloride (45.2 g, 0.4 mol) in 80 ml of diethyl ether was added slowly under vigorous stirring to control the reaction temperature of maximal 35 °C. Immediately, a colorless precipitate formed and the reaction mixture was stirred for another 30 min. Then 80 ml water and 42.4 g (0.4 mol) sodium carbonate were added. As soon as no further CO_2 production could be observed, a solution of chloroacetyl chloride (45.2 g, 0.4 mol) in 40 ml diethyl ether was added under vigorous stirring. Along with further CO_2 production, colorless crystals formed that were filtered and recrystallized (methanol); m.p. 162–163 °C (ref.:[12] 172–173 °C); yield: 40.2 g (55%).

^{1}H NMR (DMSO-d_6): $\delta = 4.18$ (s, 4 H), 10.50 (s, 2 H).

IR (KBr): 3184 (N–H), 3049 (C–H), 1610 (C=O), 794 cm^{-1} (C–Cl).

$C_4H_6N_2O_2Cl_2$ (185.00): Calcd. C 25.84, H 3.24, N 15.14; Found C 25.80, H 3.23, N 15.23.

2,5-Bis(chloromethyl)-1,3,4-oxadiazole

A mixture of 15.0 g perchloric acid (70%) and 70 g chloroacetyl chloride was heated to give a homogenous solution and 20.0 g of 1,2-bis(chloroacetyl) hydrazide (0.108 mol) were added. The reaction mixture was kept at 50–60 °C for 4 h with stirring. After cooling to room temperature, the mixture was poured into ice water. The pH of the resulting solution was adjusted with aqueous sodium carbonate solution to pH 9. The resulting oil-like liquid was extracted with diethyl ether and washed with a 10 wt.-% sodium carbonate solution. The solution was dried over anhydrous potassium carbonate, the solvent was removed to give the product as a colorless liquid; b.p. > 200 °C (decomposed); yield: 14.1 g (72%).

^{1}H NMR ($CDCl_3$): $\delta = 4.69$ (s, 4 H).

IR (film): 3029, 2971 (C–H); 1579, 1566 (C=N); 785 cm^{-1} (C–Cl).

$C_4H_4N_2OCl_2$ (167.00): Calcd. C 28.77, H 2.41, N 16.78; Found C 28.86, H 2.56, N 16.82.

Poly(1,3,4-oxadiazole-2,5-diyl-1,2-vinylene)

Tetrabutylphosphonium bromide (2.0 g) and different amounts (1, 3, 5, 8 and 10 g) of 2,5-bis(chloromethyl)-1,3, 4-oxadiazole were dissolved in 30 ml toluene. At room temperature, the solution was carefully placed onto the surface of an aqueous potassium hydroxide solution (30 wt.-%, 20 ml) and a black polymer film formed at the interface. As the reaction proceeded, the film became thicker and the surface less defined. After 2 h the polymer film was removed and washed with large amounts of methanol, water and acetone. The dried product was isolated as a dark brown and brittle solid; yield: 75–87%.

IR (KBr): 1625 (C=C), 1563 (C=N), 987 (oxadiazole), 966 cm^{-1} (C–H deformation on double bond).

$(C_4H_2N_2O)_n$ $(94.08)_n$: Calcd. C 51.07, H 2.14, N 29.78, Cl 0.00; Found: C 49.68, H 2.17, N 27.57, Cl 0.66.

Results and Discussion

The first experiment of the dehydrohalogenation of 2,5-bis(chloromethyl)-1,3,4-oxadiazole in a solution of *tert*-BuONa in tetrahydrofuran (THF) at room temperature resulted in an exothermic reaction to form a black polymeric solid. In order to control the polymerization, reaction conditions were varied, but decreasing the temperature to −40 °C did not significantly slow down the reaction rate or improve the product. Also, reduction of the reactivity of the base, EtONa instead of *tert*-BuONa, did not result in any improvement. Hence, the polymerization conditions were changed to interface polymerization with the monomer present in the organic phase (toluene), the base (KOH) in the water phase and tetrabutylphosphonium bromide as an additional phase-transfer catalyst. In this way, dehydrohalogenation of 2,5-bis(chloromethyl)-1,3,4-oxadiazole to the reactive intermediate and consecutive polymerization is limited to the interface and controlled by mass transport. The polymer obtained such indeed had higher molecular weight as compared to the one-phase reaction in THF, as could be noticed by the much higher solubility and lower viscosity of the one-phase product in concentrated sulfuric acid.

The IR spectra of all polymers obtained from interface polymerization are similar. The spectrum of the monomer

as well as the polymers display the characteristic absorption bands at 1560–1570 cm^{-1} and 980–990 cm^{-1} for the 1,3,4-oxadiazole ring,[13] with a broadening and minor shift of the bands in the polymer spectra. The vibrational modes around 1625 cm^{-1} (broad) and 966 cm^{-1} in the polymer spectra can be assigned to C=C stretching vibration and C–H out-of-plane deformation of trans double bonds, which indicates the formation of a conjugated backbone structure. However, definite assignment is difficult because of overlapping bands and broadening. Elemental analysis results are almost identical to the previous findings of Schopov et al.[11] for this polymer. Furthermore, if polymerization proceeds as depicted in Scheme 1, no chloride should be present in the polymer product and indeed only 0.66% Cl was found which can be attributed to impurities. It was reported that polycondensation of fumaramide with hydrazine sulfate in polyphosphoric acid only yields low-molecular-weight products that are soluble in some organic solvents such as dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone. In contrast to other polymers formed by polycondensation formation of 1,3,4-oxadizole polymers usually results in high-molecular-weight products. The low molecular weights observed for poly(1,3,4-oxadiazole-2,5-diyl-1,2-vinylene) were explained by immediate precipitation of the polymer and, therefore, inaccessibility of the functional groups for further polycondensation. Furthermore, the polycondensation route results in many structural defects, such as uncyclized hydrazide groups,[11] which directly limit the length of the backbone and as a consequence the conjugated system. These defects can be further converted to the 1,3,4-oxazdiazole rings by an additional heating step only partially. In other words, ring formation during polycondensation results in an incomplete conjugated polymer of low molecular weight.

In order to obtain a first hint on the molecular weight of the polymer, the viscosities of polymers prepared from different initial monomer feeds were measured at 20 °C in concentrated sulfuric acid ($c = 0.001$ g/ml). Figure 1 shows the specific viscosity ($\eta_{(sp)}/c = [(\eta_c\text{-}\eta_0)/\eta_0]/c$; average of four measurements) plotted versus the amount of initial monomer feed for the polymerization.

As the initial amount of monomer in the organic phase was increased, the $\eta_{(sp)}/c$ values of the resulting polymer increased quickly and then gradually reached a value of about 0.98×10^2 $ml \cdot g^{-1}$. Based on viscosity measurements, the poly(1,3,4-oxadiazole-2,5-diyl-1,2-vinylene) prepared was of significantly higher molecular weight as that obtained by polycondensation, which was reported to have an $\eta_{(sp)}/c$ value of around 0.046×10^2 $ml \cdot g^{-1}$.[11]

In order to investigate the reaction mechanism of the dehydrohalogenation of 2,5-bis(chloromethyl)-1,3,4-oxadiazole resulting in the conjugated polymer, possible intermediates might be captured under different reaction conditions. If the reaction were to proceed via a biradical

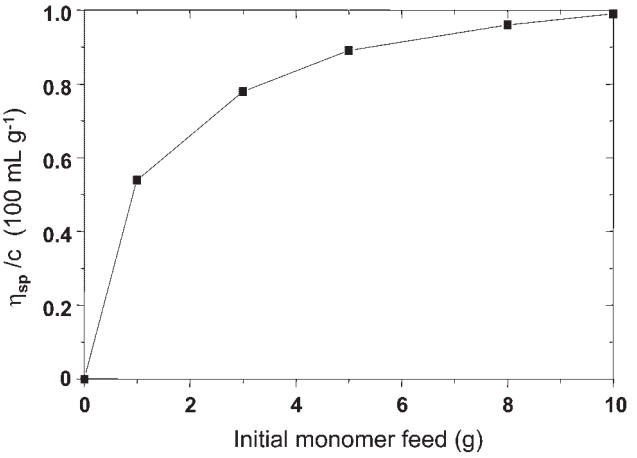


Figure 1. Initial monomer feed in interface polymerization versus specific viscosity of the resulting polymer product.

species, the presence of a protic solvent would not influence polymerization, whereas an anionic reaction route would result in different products. Hence, we performed the dehydrohalogenation of 2,5-bis(chloromethyl)-1,3,4-oxadiazole in ethanol as the solvent containing equimolar amounts of EtONa at 0 °C. Immediately, sodium chloride was formed as a white precipitate. The reaction products were isolated by careful removal of the solvent under reduced pressure. The remaining liquid was characterized by means of ^{1}H NMR spectroscopy without further purification so that all products except NaCl can be detected. Figure 2 shows the ^{1}H NMR spectrum obtained featuring minor impurities but prominent signals that can be assigned to mono-substituted 2-chloromethyl-5-ethoxy-1,3,4-oxadiazole as the only product. This can be explained by a reaction pathway as displayed in Scheme 2.

Nucleophilic replacement of Cl by an ethoxy group would result in a mixture of mono-, double- and non-substituted products which could have been identified in the NMR spectrum and, moreover, would hardly occur so rapidly at low temperature. The reaction route includes three steps: (i) dehydrohalogenation of 2,5-bis(chloromethyl)-1,3,4-oxadiazole resulting in an active intermediate, (ii) addition of EtONa to form an anionic species, and (iii) proton exchange between solvent and anionic species. In the third step the anionic polymerization of the intermediate is blocked. The reaction observed in protic solvents also excludes a radical mechanism. As compared to the dehydrohalogenation of electron-rich 1,4-bis(chloromethyl)benzene (Gilch route) the reaction of the electron-poor oxadiazole proceeds faster and easier, probably due to the alternative reaction mechanism. While the quinodimethane intermediate might react as a free biradical to the corresponding polymer, the oxadiazole intermediate follows an anionic polymerization mechanism. The aromatic moiety not only influences the mechanism of polymerization but also the stability of the resulting precursor. In the

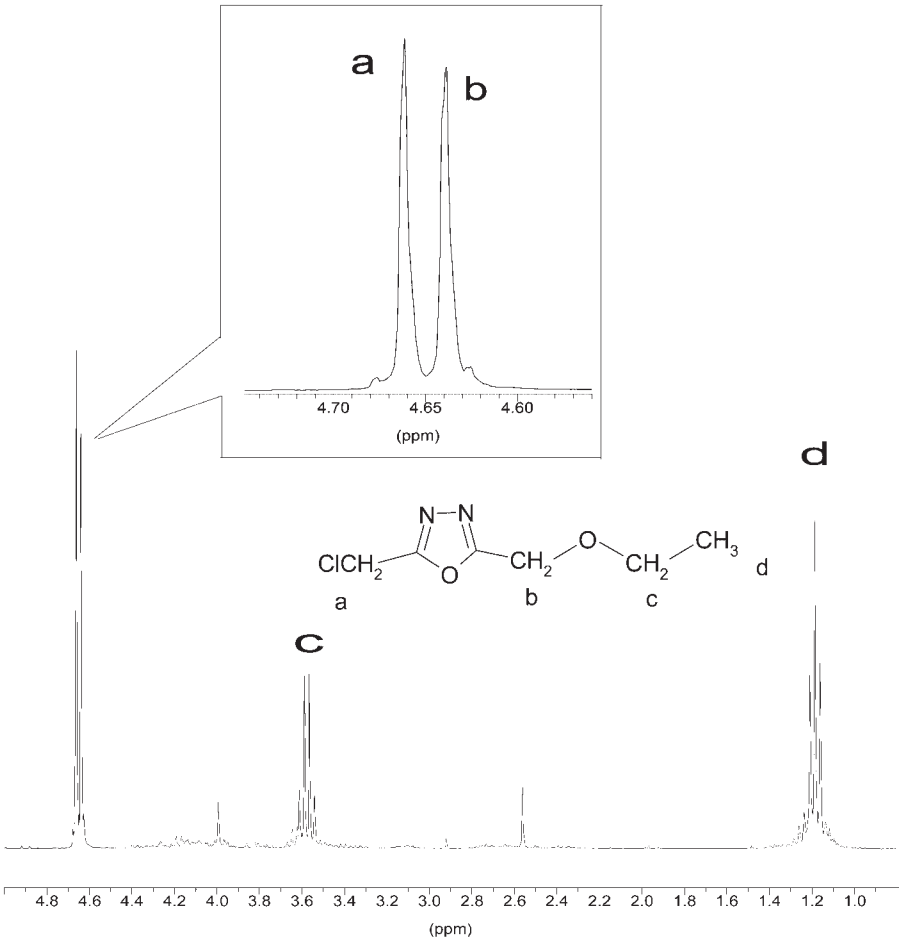
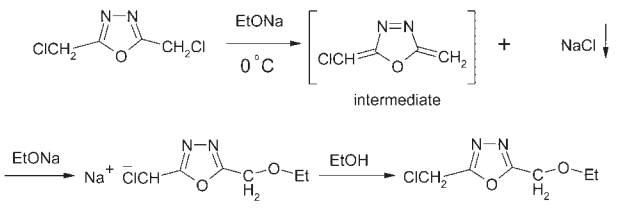


Figure 2. ^{1}H NMR spectrum of the crude reaction product of 2,5-bis(chloromethyl)-1,3,4-oxadiazole in EtOH/EtONa (cf. main text for details).

preparation of some PPV derivatives[14,15] soluble precursors could be isolated easily by controlling the amount of base. However, in the present case, it was not possible to obtain an analog precursor as the second dehydrohalogenation proceeds immediately. As a consequence and as revealed by means of elemental analysis, the Cl content in the final polymer is low.

Further studies concerning the structure of the conjugated polymer (i.e. cis or trans conformation), specific conductivity, and thermal stability are currently under investigation.



Scheme 2.

Conclusions

An alternative reaction is presented to prepare conjugated poly(1,3,4-oxadiazole-2,5-diyl-1,2-vinylene) via anionic polymerization. The resulting polymers are of significantly higher molecular weight and have less structural defects as compared to the common polycondensation route. The exothermic reaction could be controlled by performing the polymerization at the toluene/water interface in the presence of a phase transfer catalyst.

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[1] H. G. Gilch, W. L. Wheelwright, *J. Polym. Sci. A-1* **1966**, *4*, 1337.
[2] P. L. Burn, A. Kraft, D. R. Baigent, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer, A. B. Holmes, R. W. Jackson, *J. Am. Chem. Soc.* **1993**, *115*, 10117.
[3] F. Wudl, P. M. Allemand, G. Srdanov, Z. Ni, D. McBranch, *ACS Symp. Ser.* **1991**, *455*, 683.
[4] F. Wudl, S. Hoger, C. Zhang, K. Pakbaz, A. J. Heeger, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34(1)*, 197.
[5] C. Zhang, S. Hoger, K. Pakbaz, F. Wudl, A. J. Heeger, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35(1)*, 197.
[6] C. Zhang, H. Seggern, K. Pakbaz, B. Kraabel, H.-W. Schmidt, A. J. Heeger, *Synth. Met.* **1994**, *62*, 35.
[7] C. L. Gettinger, A. J. Heeger, J. M. Drake, D. J. Pine, *J. Chem. Phys.* **1994**, *101*, 1673.
[8] O. Schäfer, F. Brink-Spalink, B. Smarsly, C. Schmidt, J. H. Wendorff, C. Witt, T. Kissel, A. Greiner, *Macromol. Chem. Phys.* **1999**, *200*, 1942.
[9] [9a] O. Schäfer, F. Brink–Spalink, A. Greiner, *Macromol. Rapid Commun.* **1999**, *20*, 190; [9b] F. Brink-Spalink, A. Greiner, *Macromolecules* **2002**, *35*, 3315.
[10] A. Greiner, S. Mang, O. Schäfer, P. Simon, *Acta Polym.* **1997**, *48*, 1.
[11] I. Schopov, M. Vodenicharova, *Makromol. Chem.* **1978**, *179*, 63.
[12] A. Kreutzberger, *J. Org. Chem.* **1957**, *22*, 679.
[13] V. Sinigersky, G. Wegner, I. Schopov, *Eur. Polym. J.* **1993**, *29*, 617.
[14] W. J. Swatos, B. Gordon III, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31(1)*, 505.
[15] B. R. Hsieh, W. A. Feld, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34(2)*, 410.